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The current and potential applications of Ambient Mass Spectrometry in detecting food fraud

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The current and potential applications of Ambient Mass Spectrometry in detecting food fraud



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ABSTRACT

The adulteration of food has received substantial amounts of media attention in the last few years, with events such as the European horsemeat scandal in 2013 sending shockwaves through society. Almost all cases are motivated by the pursuit of profits and are often aided by long and complex supply chains. In the past few years, the rapid growth of ambient mass spectrometry (AMS) has been remarkable, with over thirty different ambient ionisation techniques available. Due to the increasing concerns of the food industry and regulators worldwide, AMS is now being utilised to investigate whether or not it can generate results which are faster yet comparable to those of conventional techniques. This article reviews some aspects of the adulteration of food and its impact on the economy and the public's health, the background to ambient mass spectrometry and the studies that have been undertaken to detect food adulteration using this technology.

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1. Introduction

With a growing global human population and longer life expectancies, the increased demand for food has led to corresponding growth of the food industry. In 2013 the agri-food sector contributed

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¹ Figure 1 taken from the work undertaken by Montowska et al.: M. Montowska, M.R. Alexander, G.A. Tucker, D.A. Barrett, *Anal. Chem.* 86 (2014) 10257.

Table 1

IGD grocery market size forecasts between 2015–2020 for international markets (US dollars-billions). [8]

US dollars (billions)	2015	2016	2017	2018	2019	2020
UK	310	320	328	336	344	352
United States of America (USA)	1,078	1,122	1,169	1,216	1,260	1,305
China	1,120	1,174	1,237	1,314	1,400	1,491
India	503	566	635	713	802	901
Japan	457	464	469	474	479	485
EU	1,787	1,829	1,872	1,918	1,970	2,024
North America	1,186	1,234	1,286	1,337	1,385	1,434
Asia	3,034	3,240	3,466	3,724	4,012	4,325
Total world	8,757	9,302	9,861	10,464	11,114	11,814

£103 billion to the United Kingdom (UK) economy, which accounted for 7.6% national Gross Value Added (GVA). [1] More recently, the Institute of Grocery Distribution (IGD) estimated that the UK food retail industry has a turnover of £177.5 billion in the year for May 2015, with projections for over £200 billion of sales in 2020. [2] Horizon forecasts that the UK foodservice market is worth £46.6 billion in 2014 and that this will rise to £56.3 billion in 2019. [3] On a global scale the IGD expects the value of the world's grocery market to increase by a third between 2015–2020 reaching \$11.8 trillion in 2020, with the greatest contribution in growth being driven by lower-middle income countries such as India, Indonesia and Nigeria. [4] Table 1 identifies how this value was established, showing the grocery market size forecasts for the major international markets between 2015–2020 in US dollars (billions).

The maximisation of profits is the prime target for businesses. However, within the food industry, where the majority of businesses are profitable and this profit is made by working within legal frameworks, there are some cases where profit is made illegally through the sale of fraudulent food. Food fraud is an economically motivated concept that has occurred within the food production and retail sectors since trading began. [5] It is defined as the deliberate and intentional substitution, addition, tampering or misrepresentation of food, food ingredients and food packaging for an economic gain. [6] The Grocery Manufacturers Association (GMA) of America estimates that food fraud costs the global food industry between \$10 billion and \$15 billion per year and that it affects up to 10% of all the food that is eaten in the developed world and 20% in the developing world. [7] To combat this ever growing problem, many international food standards and regulations have been introduced. The European Union (EU) food labelling directive 2000/13 article 2 requires that consumers must not be misled regarding the characteristics of food, in particular the nature, identity, manufacture, origin and quality. [5]

Economically motivated adulteration (EMA) of food often goes undetected until it is too late to rectify the issue and therefore, it can pose a substantial health risk. [9] Such is the anxiety at the moment that the World Health Organization (WHO) stated that food contamination, whether it be deliberate or accidental, is one of the major public health threats of the 21st century. [10] The impact that food adulteration can have on the public's health very much depends on what adulterant is used and the extent of any contamination. The public's health can be put at an immediate risk with the inclusion of toxic or lethal contaminants, which is known as direct food fraud. Examples of this include melamine and the substitution of olive oil with poor refined peanut oil. The harmful effects of food fraud may require a long time exposure to the adulterant such as the addition of the illegal Sudan dyes to spices; [11] this phenomenon has been described as indirect food fraud. [6]

The adulteration and fraudulent sale of food is believed to be growing at a rapidly rising rate, with all foods susceptible. Certified labels such as 'Organic' and 'Fair Trade' goods may also be affected by food fraudsters, with Europol indicating in the May 2015

edition of *The Grocer* that along with fake organic goods, which are already a growing problem in the food industry, Fair Trade fakes could be the next fraud scandal. [12] Additionally, Europol also indicated that Mediterranean countries such as Egypt and Turkey were responsible for a large share of counterfeit products within the food and drink industry coming into the EU.

Food fraud has led to many people having little faith in the authenticity of the food that they are purchasing. Consumers, authorities and the reputable food industry are now demanding greater controls on the quality of food, the authenticity and traceability of food and food safety. Reviews carried out by Ellis et al., Reid et al., Reinholds et al. and Castro-Puyana et al. signify the considerable amount of work that has been dedicated towards detecting the adulteration, authenticity, traceability, safety and quality of food. Methods of detection that have been utilised include; spectroscopic techniques such as ultraviolet-visible (UV), mid infrared (MIR), near infrared (NIR), Fourier transform infrared (FT-IR), Raman, fluorescent; nuclear magnetic resonance (NMR); isotope ratio mass spectrometry (IRMS); inductively coupled plasma mass spectrometry (ICP-MS); proton transfer reaction-mass spectrometry (PTR-MS); high performance liquid chromatography (HPLC) and gas chromatography (GC); mass spectrometry techniques coupled with chromatography such as liquid chromatography-mass spectrometry (LC-MS) and gas chromatography-mass spectrometry (GC-MS); electronic nose; DNA based technologies such as polymerase chain reaction (PCR); immunological technologies such as enzyme-linked immunosorbent assay (ELISA) and thermal techniques such as differential scanning calorimetry (DSC). [13–16] However, most of these techniques require long and complex sample preparation and assay times. Ambient mass spectrometry (AMS) is a relatively new field of analytical chemistry which has the potential to overcome these issues, whilst giving results that are comparable with other conventional techniques.

2. Ambient mass spectrometry (AMS)

Liquid chromatography-mass spectrometry (LC-MS) has long been utilised to investigate metabolic profiling of animal, human and plant tissues. [17,18] Ionisation techniques such as electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI) have worked very well in separating analytes from a solution-phase matrix at atmospheric pressure and transferring free ions into a vacuum environment ready for mass spectrometry (MS) analysis. [19] However, an issue with all atmospheric pressure ionisation sources is the long, often complex and expensive sample preparation time.

2.1. The creation of AMS

AMS was first identified in 1998 when Fenn, in his patent, anticipated paper spray mass spectrometry (PS-MS) when describing a direct ionisation method employing cellulose based materials. [20] However, the first published work by Wang et al. using PS-MS did

Table 2

Applications of desorption electrospray ionisation (DESI), direct in real time analysis (DART) and the atmospheric analysis probe (ASAP)

Ambient ionisation technique	Applications	References
Desorption electrospray ionisation (DESI)	Forensics, public safety, explosives, toxic industrial compounds, chemical warfare agents, pharmaceuticals, industrial polymers, small organic molecules, proteins, oligonucleotides, carbohydrates and food analysis.	[22,24,27]
Direct in real time analysis (DART)	Chemical warfare agents, pharmaceuticals, metabolites, peptides, oligosaccharides, synthetic organics, organometallics, drugs of abuse, explosives for forensics and security, toxic industrial chemicals, food analysis and medicinal analysis	[25]
Atmospheric pressure solid analysis probe (ASAP)	Pharmaceuticals, drugs, nucleosides, polymers, coal-related model compounds, steroids and food analysis	[26,28,29]

not occur until 2010 and as a result desorption electrospray ionisation (DESI) is widely regarded as the first ambient ionisation technique to be created in 2004 by *Takats et al.* [21, 22] Their new ionisation technique allowed samples to be analysed direct and rapidly in the open air, with no sample preparation required. [23] *Takats et al.* initially stated that DESI was capable of analysing proteins and protein complexes, carbohydrates, oligonucleotides, industrial polymers and small organic molecules. [24] The research group observed that the protein DESI spectra were identical to that of ESI spectra, establishing that the results obtained from the DESI source were comparable with that to conventional techniques such as LC-MS. In 2005, two more ambient mass spectrometry techniques were published; *Cody et al.* introduced direct analysis in real time (DART) and *McEwen et al.* created the atmospheric pressure solid analysis probe (ASAP). [25, 26] Table 2 identifies the present applications of the three ambient ionisation techniques, which range across various industries including pharmaceuticals, forensics and chemical warfare agents.

2.2. The mechanisms and evolution of AMS

Further development of ambient ionisation techniques has been undertaken to the point now where there are over thirty different techniques available. [30] Ambient ionisation techniques can be classified into three groups based upon their different ionisation mechanisms; (1) Spray or jet ionisation technique such as DESI where charged droplets are produced from an electrospray needle at a high voltage; (2) Electric discharge ambient ionisation technique, such as DART where ions, electrons and metastable atoms are produced using helium/nitrogen and a corona discharge; (3) An ambient gas-, heat- or laser assisted desorption/ionisation technique such as ASAP where a solid or liquid sample is ionised at atmospheric pressure between (300°C–500°C). [31]

Table 3 outlines which ambient ionisation techniques are characteristic of the three mechanisms described previously. Under the mechanism of spray or jet ionisation is a technique known as desorption electrospray/metastable-induced ionisation (DEMI). This technique, according to *Nyadong et al.* integrates the benefits and circumvents the limitations of DESI and (DART)-type metastable-induced chemical ionisation (MICI). [32] As a result, it can be operated in three different ionisation modes; (i) a spray or jet ionisation: DESI; (ii) a metastable –induced chemical ionisation (MICI): DART; (iii) a multi-mode: DEMI. [32] Therefore, although Table 3 has DEMI situated under the ionisation mechanism of spray or jet ionisation, theoretically it can also reside under electric

Table 3

The grouping of ambient ionisation techniques based upon their ionisation mechanisms

Spray or jet ionisation	Electric discharge ambient ionisation	Ambient gas-, heat- or laser assisted desorption/ionisation
Desorption electrospray ionisation (DESI)	Atmospheric pressure glow discharge desorption ionisation (APGDDI)	Atmospheric solid analysis probe (ASAP)
Desorption atmospheric pressure photo ionisation (DAPPI)	Desorption atmospheric pressure chemical ionisation (DAPCI)	Electrospray-assisted laser desorption ionisation (ELDI)
Desorption electrospray/metastable induced ionisation (DEMI) ^a	Direct analysis in real time (DART)	Extractive electrospray ionisation (EESI)
Desorption sonic-spray ionisation (DESSI) / Easy ambient sonic-spray ionisation (EASI)	Dielectric barrier discharge ionisation (DBDI)	High –voltage-assisted laser desorption ionisation (HALDI)
Electrode-assisted desorption electrospray ionisation (EADSI)	Desorption corona beam ionisation (DCBI)	Infrared laser ablation metastable-induced chemical ionisation (IR-LAMICI) ^a
Electrostatic spray ionisation (ESTASI)	Helium atmospheric pressure glow discharge ionisation (HAPGDI)	Laser ablation electrospray ionisation (LAESI)
Jet desorption electrospray ionisation (JeDI)	Liquid sampling-atmospheric pressure glow discharge (LS-APGD)	Laser desorption spray post-ionisation (LDSPI)
Liquid extraction surface analysis (LESA)	Low temperature plasma (LTP)	Laser spray ionisation (LSI)
Paper spray (PS)	Microwave induced plasma desorption ionisation (MIPDI)	Matrix assisted laser desorption electrospray ionisation (MALDESI)
Transmission mode desorption electrospray ionisation (TM-DESI)	Plasma assisted desorption ionisation (PADI)	Rapid evaporative ionisation mass spectrometry (REIMS)

^a Indicates that both DEMI and IR-LAMICI ionisation mechanisms have traits similar to that of an electric discharge ambient ionisation mechanism and can therefore be grouped in two different ionisation mechanism classes.

discharge ambient ionisation. Additionally, infrared laser ablation metastable-induced chemical ionisation (IR-LAMICI) is also characteristic of two of the ionisation mechanisms, as described by *Galhena et al.* when they stated that IR-LAMICI integrates both IR laser ablation and direct analysis in real time (DART)-type metastable-induced chemical ionisation. [33] Firstly, IR laser pulses impinge the sample surface ablating surface material and then a portion of ablated material reacts with the metastable reactive plume facilitating gas-phase chemical ionisation of analyte molecules generating protonated or deprotonated species in positive and negative ion modes, respectively. [33]

3. The analysis of food adulteration using AMS

Most, if not all of the food commodities that appear on the shelves of supermarkets are either susceptible or have already been exposed to some form of food fraud. With greater controls and tests being demanded by the authorities and food industry, analytical techniques already play a key role in detecting the adulteration of food. Table 4 summarises the issues that have been addressed within a number of different food commodities using conventional techniques. Additionally, the table also outlines which of these issues have or have not been assessed using AMS. However, what this table does not address is the ability or indeed inability of AMS techniques to detect the adulteration in a fit for purpose manner. AMS continues to evolve and some of the techniques have excelled and been proven to produce accurate and reproducible results, whilst

Table 4

The issues within food analysis that have been addressed by ambient mass spectrometry and conventional techniques since 2009

Food and drink commodities	Issue(s) addressed/analysed using ambient mass spectrometry (AMS)	Ambient mass spectrometry (AMS) techniques	Issue(s) addressed/analysed using conventional techniques	Conventional techniques	References
Meat	Meat speciation/authentication; chicken feed control; Triacylglycerol (TAG), diacylglycerol (DAG) and free fatty acid (FFA) profiles of dry-cured ham	DART-MS, LESA-MS, DESI-MS, PS-MS, EASI-MS	Meat authentication/adulteration; mycotoxins in chicken feed	Stable ratio analysis, PCR, ELISA, NIRS, Raman, LC-MS	[34–46]
Fish	Dietary supplementation; geographic profiling of dried sea cucumber; lipidomic profiling of caviar; analysis of sardine, trout and sardine	DART-MS, DAPCI-MS, EASI-MS	Frozen/fresh differentiation; fish authentication/ mislabelling; mycotoxins in fish feed	Raman, PCR-ELISA, FT-(N)IR, LC-MS, NMR, GC-MS	[47–56]
Milk	Identification of melamine, dicyandiamide and cyanuric acid in milk powder, liquid milk, condensed milk and soy milk; animal species origin	DAPCI-MS, DESI-MS, DART-MS, LTP-MS	Milk authenticity; animal species origin; adulteration of soy milk and yak milk	TD-NMR, MIR, PCR, NIRS, ELISA	[57–67]
Dairy products	Butter cholesterol levels; cheese adulteration with plant oils; analysis of margarine	DAPPI-MS, DESI-MS, DART-MS	Cheese adulteration; butter adulteration	LC-MS, NMR	[59,68–71]
Herbs, spices and sauces	Addition of illegal dyes and additives; geographic discrimination of star anise; cinnamon authentication.	DAPCI-MS, DESI-MS, ASAP-MS, DART-MS, PS-MS	Contaminant analysis and adulteration in herbs and spices; Pesticides in herbs	NMR, ICP-MS, UV/Vis, NIRS, Raman, FT-IR, LC-MS, GC-MS	[15,29,35, 72–80]
Oils, nuts and condiments	Olive oil adulteration; geographic profiling of olive oil; quantitative analysis of 5-hydroxymethylfurfural in honey; fingerprinting of yoghurt	DART-MS, EASI-MS, LDSPI-MS, PS-MS	Adulteration of olive and argon oils; analysis of balsamic vinegar; authenticity of hazelnuts	GC-MS, electronic nose, NMR, NIRS	[81–88]
Cereals	Mycotoxins and pesticides in cereals	DART-MS	Mycotoxins in wheat; herbicides in maize; pesticides in corn, oat, rice and wheat	LC-MS/MS, GC-MS, ELISA	[89–92]
Fruit and vegetables	Pesticides in fruit and vegetables; differentiation of organically and conventionally grown peppers and tomatoes	LTP-MS, PS-MS, LC/DBDI-MS, DART-MS	Identification of animals in vegetarian food; metabolic profiling of fruit; pesticides in fruit	PCR, NMR, LC-MS	[93–99]
Drinks	Recognition of beer brands; fungicides in wine; analysis of cola; origin and post-harvest methods of coffee beans; analysis of sports drinks	DART-MS, LTP-MS, PS-MS, EASI-MS, DESI-MS	Brandy adulteration, wine adulteration; authenticity of whiskey; ground coffee adulteration; pesticides in tea	Fluorescence spectroscopy, stable isotope ratio, IRMS, electronic nose, GC/MS, NIRS, MIRS, LC-MS	[35, 100–110]

others have fallen short. This review attempts to identify the most recent work carried out using AMS, providing various scenarios where the technique(s) have worked very well, the technique(s) which have shown indications of their potential and others where the technique(s) have not produced data of much promise.

3.1. Desorption electrospray ionisation-mass spectrometry (DESI-MS)

DESI-MS has mostly been applied to quality control plus pharmaceutical and forensic analysis due to its ability to screen samples directly and rapidly and analyse specimens in different forms (tablets, gels etc.). [27,111] Compared to conventional LC-MS, the literature indicates very little research has been undertaken regarding the detection of food adulteration using DESI-MS. Various issues have been addressed with regards to the analysis of food including the analysis of lipids in butter products, the identification of triglycerides (TG) in edible oils and margarine and the differentiation of post-harvest methods of coffee beans. [68,69,105] However, what work that has been carried out using DESI-MS has indicated that it is not particularly effective at detecting food adulteration compared to other ambient mass spectrometry techniques, with the lack of chromatographic separation being cited as the main issue.

Yang et al. attempted to detect the adulteration of milk using desorption atmospheric pressure chemical ionisation-mass spectrometry (DAPCI-MS), but they also investigated how DESI-MS could be used and how the results compared. [57] Whereas the ionisation mechanism of DESI is characteristic of ESI, the ionisation mechanism of DAPCI is more akin to that of APCI. The literature suggests that DAPCI-MS is potentially more suited to detecting the adulteration of food compared to DESI-MS, as Chen et al. showed when investigating the adulteration of tomato sauce with Sudan dyes. [72] At the outset of their study, Yang et al. gathered a DAPCI-MS spectrum of authentic melamine (10ng) and found the mass ion at m/z 127 and the fragment ions at m/z 110, 85 and 60. They then

tested powdered milk samples contaminated with melamine and found both the parent and daughter ions of this compound. However, when they utilised DESI-MS on a 10 μ L milk sample containing 10 ppm melamine, the melamine daughter ions were not picked up and instead ions of m/z 109, 84 and 81 were detected. It was concluded that DESI-MS could not be used to detect melamine contamination at a meaningful concentration. It is important to note that Yang et al. found that by drying the liquid milk samples at 120°C, they could detect weak melamine signals with the correct daughter ions using DESI-MS. Although, having undertaken this research, they still stated that powdered milk should not be directly analysed by an open-air DESI source because the fine particles started to contaminate the source region when the gas pressure was higher than 0.2 MPa.

A summary of the work using DESI-MS, with particular reference to food analysis ranging from the addition of Sudan dyes in tomatoes and spices, to the addition of sweeteners and food forensics, including the work undertaken by Yang et al. was carried out by Nielen et al. [27] Their findings suggested that due to the lack of sample preparation and therefore lack of chromatographic separation, DESI-MS is vulnerable to false-positive and false-negative findings compared to conventional LC-MS and therefore, it is not reliable enough to be used in the detection of food fraud. [27]

3.2. Direct analysis in real time-mass spectrometry (DART-MS)

Compared to DESI-MS, there is substantially more literature suggesting that DART-MS is capable of analysing food samples. However, the majority of the published work is not centred on investigating the adulteration of food but rather on how well DART-MS adapts to different situations. An example of this type of study was undertaken by Rahman et al. who attempted to use DART-MS to locate the bioactive components of curcumin present in turmeric rhizomes. [112] The researchers were able to apply DART-MS to locate the curcumin present in the pitch of the turmeric rhizomes. These

can now be extracted and added to curries and other dishes to retain the beneficial effects whilst not making the food unpalatable due to the colour or odour.

Whereas *Nielen* et al. stated that DESI-MS is inadequate at detecting food fraud, some of the literature suggests that DART-MS is much more efficient in such applications. Most of the work that has been carried out using DART-MS to detect the adulteration of food appears to have been led by the research group of Jana Hajslova, Tomas Cajka and Lukas Vaclavik who have attempted to detect adulteration in many different food and drink items with varied degrees of success. [100,113]

3.2.1. Chicken feed

Cajka et al. investigated whether DART-MS, along with multivariate data analysis, could be utilised to assess the control of chicken feed fraud. Chicken feed normally consists of wheat, corn and soya meal along with other minor components such as barley and oat. [34] Their aim was to investigate if DART-MS could differentiate between chickens that had been fed with and without chicken bone meal using metabolomics. Polar and non-polar extracts of chicken muscle were analysed in both DART (+) and DART (–). After analysis of the data *Cajka* et al. decided to only analyse polar extracts in DART (+) and non-polar extracts in DART (–) as they provided the most complex fingerprints which were subsequently used in the analysis of a large series of chicken samples. [34] Three dominating ions were detected in the polar extracts; creatine, carnosine and anserine, whilst fatty acids (FA) were detected in the non-polar extracts.

Using both principal component analysis (PCA), an unsupervised technique, and orthogonal partial least squares-discriminant analysis (OPLS-DA), a supervised technique, *Cajka* et al. were able to clearly demonstrate that by using DART-MS, they could differentiate between chickens that had been fed with chicken feed and chicken bone meal and chickens that had been fed with just chicken feed, with both polar and non-polar fingerprints able to show this.

3.2.2. Dairy products

Dairy products are extremely susceptible to food fraud, [114] with the Chinese milk scandal in 2008 being the most high profile case to date with the addition of melamine. The rationale for this addition was the fact that milk prices are dictated by their nitrogen content. Melamine contains 67% nitrogen by mass and therefore, when added to milk it enhances the milk's nitrogen content and thus the price. DART-MS, along with other AMS techniques such as DAPCI-MS and low temperature plasma-mass spectrometry (LTP-MS), [57,62] is a technique which has been utilised to detect the presence of melamine in milk powder. However, early studies identified an issue due to spectral/isobaric interferences. *Dane* et al. investigated the ionisation mechanisms of melamine using both helium and argon as the DART gas. [60] When using helium, the research group identified the formation of protonated 5-hydroxymethylfurfural (5-HMF). Protonated 5-HMF (m/z 127.0395) is a compound which has the same nominal mass to that of melamine (m/z 127.0732) which according to the research group results in clear spectral interferences. Additionally, *Dane* et al. observed that the relative abundance of 5-HMF increased with prolonged exposure to the DART heat source. As a result, the team attempted to repeat the experiments using argon as the DART gas, in combination with acetylacetone and pyridine reagent gases. The reasoning for this combination of gases was; (1) 5-HMF and more importantly melamine were not directly ionised by argon DART gas and (2) the combination of gases selectively ionised melamine whilst reducing the spectral interferences of 5-HMF. The ionisation mechanism started with a penning ionisation of acetylacetone resulting in cation radicals which when protonated form protonated acetylacetone. The proton transferred to pyridine which was then finally transferred to melamine. An important conclusion from *Dane*

et al. was that although qualitatively melamine could be detected in milk powder samples, quantitatively much more work was required. [60]

Further publications using DART-MS to detect melamine in milk powder have been produced, an example being the work undertaken by *Vaclavik* et al. who could detect the presence of melamine and cyanuric acid at levels as low as 170 $\mu\text{g/kg}$ and 450 $\mu\text{g/kg}$ respectively. [61] Additionally, the limits of quantitation (LOQ) were 450 $\mu\text{g/kg}$ for melamine and 1200 $\mu\text{g/kg}$ for cyanuric acid. Interestingly, the research group used isotopic labelling ($^{13}\text{C}_3$ –MEL and $^{13}\text{C}_3$ –CYA) to obtain accurate quantification. However, an important observation was that deuterated melamine analogues such as MEL- d_6 were found not to be suitable for quantitative analysis. [61] *Vaclavik* et al. compared the LOQ for DART-time of flight mass spectrometry (DART-TOFMS), LC-MS/MS and ELISA when analysing melamine in dried milk, condensed milk and dried cheese samples. The team stated that there was good agreement between DART-TOFMS and LC-MS/MS for the dried milk samples, but large differences for the condensed milk and dried cheese samples. The work undertaken by the research group demonstrated that AMS has many benefits such as lack of sample preparation, quick assay running times and fairly comparative qualitative results to that of conventional techniques. However, quantitatively conventional techniques such as LC-MS are still much better suited.

Another means of fraud in milk is the substitution of milk from one species with milk from another species. *Hrbek* et al. undertook the task of using DART-high resolution mass spectrometry (DART-HRMS) to investigate whether it was possible to discriminate between organic cow's milk, conventional cow's milk, goat's milk and sheep's milk. [59] When this group applied PCA to the data of all the milk samples, they made a very interesting observation. The PCA plot showed that cow's milk from both organic and conventional production were very different to sheep's milk and goat's milk. However, sheep's milk and goat's milk could not be differentiated using DART-HRMS. *Hrbek* et al. believed this occurred as the differences caused by the variability in TAG profiles were apparently larger than the inter-species differences. [59] Other interesting observations were that it was not possible to distinguish between cow's milk from organic and conventional production. However, it was possible to discriminate between cow's milk and milk from other species using DART-HRMS. This demonstrated that ambient mass spectrometry has the ability to be utilised as a tool for the detection of at least some forms of food and drink adulteration.

Additionally, *Hrbek* et al. also wanted to further test DART-HRMS and see whether it could be used to detect plant oils in milk-based foods. In order to do this, they prepared soft cheese samples with and without rapeseed, sunflower and soybean oil. The soft cheeses were made using randomly selected cows' milk. TAG compositions in milk fat, whether it be from cow, goat or sheep are much lower compared to plant oils. Therefore, when DART-HRMS was used to detect the adulteration of soft cheese with plant oils, it was able to clearly detect the plant oil even to levels as low as 1 % (w/w). According to *Hrbek* et al. between the mass range of m/z 840–910 is where there is the largest contrast between authentic soft cheese and soft cheese adulterated with plant oil can be observed, due to the presence of plant $[\text{M} + \text{NH}_4]^+$ TAGs adduct ions.

3.2.3. Olive oil

One of the most commonly adulterated food items are oils and in particular olive oil. This is a highly appreciated product worldwide and is the major lipid component of the Mediterranean diet. [82] Its unique taste and flavour makes it a very desirable product and therefore it has a high price, especially the virgin products. The adulteration of olive oil has been studied extensively with many analytical techniques such as NMR, LC-MS, supercritical fluid chromatography-mass spectrometry (SFC-MS) and

gas chromatography-mass spectrometry (GC-MS), but the sample preparation time in all cases is lengthy. [115–117]

There are many different grades of olive oil available, but extra virgin olive oil is the most sought after and therefore, the most expensive. As a result, it is very susceptible to adulteration. Vaclavik et al. utilised DART-MS to detect the adulteration of extra virgin olive oil with the cheaper hazelnut oil. [81] This group gathered their data using DART-TOFMS. Using linear discriminant analysis (LDA), Vaclavik et al. were able to detect down to 6% adulteration of extra virgin olive oil with hazelnut oil. [81] Characteristic DART-MS fingerprints in the polar TAG fractions helped identify the presence of hazelnut oil, with the time required to analyse one sample being below one minute.

3.2.4. Spices

Spices are commodities which have received substantial amounts of media attention in the last couple of years, and as result the spice industry is taking fraud very seriously. Avula et al. undertook the challenge of using DART-TOFMS and PCA to investigate the authentication of true cinnamon. [74] The samples they analysed were; *Cinnamomum verum* (true cinnamon); *Cinnamomum aromaticum* (cultivated in Southern China and Burma); *Cinnamomum loureirii* (cultivated in Vietnam) and *Cinnamomum burmanini* (cultivated in Indonesia and the Philippines). The research group obtained their data in positive mode and they identified clear groupings which were unique for each type of cinnamon. Between m/z 130–170 were phenylpropane compounds whilst between m/z 195–240 there were sesquiterpene compounds. There were clear differences in the DART-MS spectral data of the various cinnamon species and clear separation in the PCA plots, which according to Avula et al. was due to the varying intensities of coumarin, cinnamaldehyde, methyl cinnamate, aminocinnamic acid and three sesquiterpenes. [74] This work demonstrated that ambient mass spectrometry has a very important role to play in improving the traceability and authentication of food.

When the adulteration of a food or drink commodity is undertaken, the consumer's health is seldom if ever taken into account by the fraudster. In some cases, the adulteration of food can have serious health implications, such as the case in the Chinese milk scandal. Work undertaken by Shen et al. demonstrated such a case where the power of techniques such as DART-MS can be effectively utilised.

Using DART-HRMS Shen et al. investigated whether they could identify the presence of anisatin in Japanese star anise rapidly. A carpel of star anise was held in position for 15–25 s and measurements were taken in both positive and negative mode. The resulting spectra showed the clear presence of anisatin in Japanese star anise with the signals being greater than 1000 times in intensity compared to that of the Chinese star anise. The main marker of anisatin in positive mode was identified at m/z 346.148 which was the $[M + NH_4]^+$ adduct and in negative mode the marker was identified at m/z 327.107 which was the $[M-H]^-$ adduct. [73] Shen et al. stated that even though both ionisation modes clearly identified the presence of anisatin in Japanese star anise, the spectra produced in negative mode were higher in terms of sensitivity and had less interference.

As well as identifying clear spectral differences between Chinese star anise and Japanese star anise, Shen et al. also investigated whether it was possible to detect the presence of Japanese star anise in herbal teas that commonly contain star anise. Shen et al. spiked tea samples with Japanese star anise at concentrations of 0%, 1%, 2%, 5%, 20% and 50%. By dipping a glass rod into the tea so that approximately 2 μ L was analysed, the researchers were able to produce calibrations and establish that adulteration at levels as low as 1% (w/w) were measurable. When carrying out a small retail survey on eight herbal teas purchased in the Netherlands, no anisatin was

found. However, the work undertaken by Shen et al. demonstrated the importance of combating food adulteration in terms of protecting the public's health.

3.3. Atmospheric solid analysis probe-mass spectrometry (ASAP-MS)

Similar to DESI-MS, there is a scarcity of evidence to suggest that ASAP-MS has been utilised to detect the adulteration of food, but much more widely applied to the field of pharmaceuticals and the analysis. [28] Fussell et al. carried out an assessment on how ASAP had been utilised in food analysis. [29] Their main focus was on detecting pesticides in cereals and the detection of illegal dyes in spices.

With regards to work on spice fraud, most of the literature has been focused on the addition of Sudan dyes which are banned within the EU due to their carcinogenicity. However, there are many other illegal dyes such as malachite green and orange II available that have been found to be added to food items. Fussell et al. utilised ASAP-TOFMS to detect the presence of the illegal dye auramine in saffron, which is one of the most expensive spices available on the market. The ASAP probe was stirred into the sample and desorbed. The resulting ASAP-TOFMS spectrum produced an ion at m/z 268.1805 which corresponded to auramine $[M + H]^+$. The results from the ASAP probe were in agreement with results produced using LC-MS/MS, which verified the presence of auramine at 8 mg/kg. [29] Fussell et al. also stated that the ASAP probe had been used to detect the presence of bixin and norbixin in paprika, which are EU approved food additives, [118] and coumarin in cinnamon. [29] Coumarin, although found naturally in cinnamon as described previously, is also permitted to be used as a food additive. However, after investigation by the European Food Safety Authority (EFSA), a daily intake limit of 0.1 mg/kg bodyweight was set because repeated high intakes of coumarin can lead to liver failure. [119]

Work was undertaken by Waters Corporation to investigate whether the ASAP probe along with a triple quadrupole (TQD) mass spectrometer could be utilised to detect melamine in a range of milk based food products. [120] 1 μ L of milk, infant formula, or the supernatant from chocolate or biscuit were shaken with acetonitrile and directly loaded into onto the ASAP probe. The experiments were conducted in positive mode and a hot stream of nitrogen gas (400°C) was used. According to Waters, within 2.5 minutes the ASAP probe and TQD were able to screen for the presence of melamine at levels which were relevant to legislation in a range of sample matrices. Waters Corporation set the TQD in multiple reaction monitoring (MRM) mode allowing them to acquire three transitions. Similar to the work undertaken by Yang et al. Waters Corporation identified the melamine mass ion of m/z 127. The fragment ions identified using the ASAP probe were m/z 110, 68 and 60, whilst in the work undertaken using DAPCI-MS, the fragment ions identified were m/z 110, 85 and 60. [57,120] A study investigating the fragmentation of melamine was undertaken by Ju et al. where they identified that m/z 85 and 68 were both fragments of melamine, with m/z 85 being $[C_2N_2H_5]^+$ and m/z 68 being $[C_2N_3H_2]^+$. [121] Although Waters Corporation identified fragments of melamine, there was no information regarding which, if any, food items were contaminated with melamine. Overall, ASAP-MS provides good qualitative results, but with regards to quantitative results, the technique struggles and is therefore potentially insufficient at detecting the adulteration of food.

3.4. Other ambient mass spectrometry techniques

Since the development of the three original ambient ionisation techniques; DESI, DART and ASAP, there are now a broad range of different ambient ionisation techniques which when coupled with mass spectrometry show potential for food applications. However, most of the published techniques that have been utilised were in

the area of pharmaceutical sciences. In much of the literature assumptions have been made that because the technique performs well in one area of analytical science then it must be employed in a different area; i.e. food safety. An example of this was shown in a paper by Ren et al. where they utilised high-voltage-assisted laser desorption ionisation-mass spectrometry (HALDI-MS). They established that HALDI-MS was capable of analysing liquid samples including proteins, pharmaceuticals and other biological fluids in both positive and negative mode. [122] They went on to state that the technique could be further developed to aid the rapid analysis of food, however, to date there is no literature concerning the use of HALDI-MS to investigate food analysis. Potentially, HALDI-MS may be similar to DESI-MS in that they both produce very accurate and reliable results in applications such as pharmaceuticals, but in terms of food analysis they may both suffer the same shortfalls.

3.4.1. Easy Ambient Sonic-spray Ionisation-mass spectrometry (EASI-MS)

EASI-MS is another AMS technique that has been used fairly extensively to investigate food quality and authenticity issues as demonstrated in a review carried out by Porcari et al. [123] Olive oil fraud through adulteration with cheaper oils and the detection using DART-TOFMS has previously been discussed. Another form of fraud is based on geographic origin of foods that are labelled as originating from one country but instead originate from another. Therefore, it is essential that there are analytical techniques that can be utilised to detect differences between olive oils originating from different countries, hopefully through the identification of unique markers. Riccio et al. utilised EASI-MS to investigate whether it was possible to discriminate between thirty different olive oil samples which had originated from Portugal, Italy, Spain, Greece and Lebanon. [82] EASI works by forming charged droplets which are produced due to sonic spray which causes a statistical imbalance discharge of charges. [124] It is thought that EASI is the simplest ambient ionisation technique since only a compressed gas (nitrogen or air) is required and it does not require high voltages, UV lights, laser beams, corona or glow discharges or heating. [124] Additionally, EASI has the ability to produce positive and negative ions simultaneously.

Riccio et al. utilised EASI-TOFMS and acquired their data in negative mode. Air dried extracts were obtained using 0.3mL oil and 1mL (methanol: water) (1:1) solution. Droplets were then placed on the sample spot and allowed to dry. [82] Using chemometrics Riccio et al. were able to clearly discriminate between the samples based on their geographic origins. Additionally, it was also possible to discriminate between the samples according to their FA ratios based on a set of four ions of m/z 255, 279, 281 and 283. Another important observation was that olive oil samples originating from Spain contained the greatest relative abundance of phenols, whilst the samples originating from Lebanon contained the lowest. Unfortunately, the researchers were not able to identify unique markers for all the olive oils except for the samples originating from Lebanon with the ion of m/z 564 present in only the Lebanese samples.

Caviar is a luxurious product which the public are willing to pay a high premium for. However, the fast natural degradation of the product presents issues when shipping it around the globe. As a result, conservation protocols such as salting and pasteurisation are carried out to preserve the product, although pasteurisation is believed to reduce the culinary and economic value of caviar. Due to the high price of this luxurious product, it is susceptible to food fraud with salted caviar being substituted with pasteurised caviar. Porcari et al. investigated whether it was possible of differentiating the two types of caviar based upon their lipid profiles. [49] In their work three mass spectrometry techniques were utilised, with EASI-MS coupled with thermal imprinting (TI) being one of them.

Caviar samples (500mg) were analysed on an envelope paper with a solution of methanol: chloroform (2:1, v: v) being dripped on the sample surface. Using a halogen bulb, the lipid fraction had thermally imprinted on the envelope, ready to be analysed by EASI-MS in positive mode. With the samples being run at both room temperature and 4°C, Porcari et al. stated that there were clear spectral differences between the two types of caviar at 4°C which was due to the relative abundances of m/z 828 (phosphatidylcholines (PC)) and m/z 927 (TAG) with pasteurised caviar having a greater abundance of m/z 927 and salted caviar m/z 828. [49] The overall conclusion stated by the research group was that TI-EASI (+) -MS was capable of comprehensive lipid profiling as both PC and TAG ions could be simultaneously analysed.

3.4.2. Paper spray-mass spectrometry (PS-MS)

To some PS-MS is regarded as the first ambient mass spectrometry technique to have been created. Paper spray ionisation operates by applying a high voltage to a paper triangle wetted with a small volume of solution. When the high voltage is applied, the ionisation is characteristic of an ESI process and charged droplets are generated. The literature suggests that much work has been dedicated towards the analysis of food using PS-MS. A review carried out by Zhang et al. demonstrated some of the work that had been undertaken, including the identification of clenbuterol, terbutaline, salbutamol and ractopamine in beef and pork, melamine in milk powder and infant formula, Sudan dyes in chilli powder and plasticizers in sports drinks. [35] Additionally, another review undertaken by Klampfl et al. demonstrated that since 2010, food commodities such as olive oil, spices, beverages and caramel have been investigated using PS-MS. [125] The technique has also been utilised to analyse cola and identify the presences of pesticides in fruit and vegetable products. [94,103]

Coffee is a commodity which is of huge importance to developing countries as it is produced mostly in Asia, Africa and Central and Southern America. In 2014 Brazil was the largest producer of coffee and according to the International Coffee Organization it was also the largest exporter in July 2015. [126,127] Most coffee is consumed in developed countries, with the EU and the USA being responsible for 86% of total coffee imports. [128] Garrett et al. undertook the challenge of investigating whether or not it was possible to geographically discriminate between coffee beans which had originated from three different regions in Brazil using PS-MS. [104] The research group obtained arabica coffee beans from Bahia, Rio de Janeiro and Paraná. The coffee beans were extracted in a methanol: water solution (9:1) and then 5µL was spotted onto a triangular shape paper. Measurements were carried out in both positive and negative mode, but after initial review Garret et al. established that the spectra in negative mode were dominated by high background peaks and as a result, they only used the positive mode data. Using PCA and hierarchical cluster analysis (HCA), the research group identified three clear groupings which represented the three different geographic origins of the coffee beans. The reasoning behind the groupings was not due to identification of unique geographic markers, but instead the varying intensities of the ions.

3.4.3. Laser desorption spray post-ionisation-mass spectrometry (LDSPI-MS)

The coupling of laser desorption and ESI post-ionisation is a popular combination which has led to the creation of techniques such as ELDI, LSI, LAESI, and MALDESI. In reality, there is very little difference between these techniques, with the main point of distinction being the type of laser that is used (UV, IR, Nd:YAG, etc.). The popularity of laser based techniques is down to the fact that spatial resolution is achieved and multiply charged ions are freely generated. With regards to food analysis, LDSPI-MS has not really played a key role, bar the work undertaken Liu et al. [83] who

investigated whether it was possible to differentiate between yogurt brands based on unique fingerprints. In their work, the research group utilised a Nd:YAG laser (wavelength of 1064nm) and irradiated the samples, which were deposited on a gold surface at 45° angles. A solution of methanol: water (1:1, v: v) was introduced through a spray emitter at a flow rate of 0.2μL/min.

The research group attempted to differentiate three different brands of yogurts; Erhmann, Guangming and Yili. Working in positive ion mode, Liu et al. obtained spectra that showed clear visible differences between the three yogurt brands. A PCA score plot of the data emphasised those differences, with three clear groupings, each one representative of the three different yogurt brands. This work showed glimpses that laser based AMS techniques may have a key role to play in tackling food fraud. It must also be stated that MALDESI has been also been utilised in some sort of capacity to analyse food. However, this work was carried out using a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. [129] Although the work undertaken by Liu et al. is encouraging, it is still some time off before it can be stated that laser based AMS techniques provide 100% accurate and reliable results with regards to detecting the adulteration and fraudulent sale of food.

4. The analysis of meat adulteration using AMS

Meat is often shown to be one of the most vulnerable commodities, particularly processed meats to food adulteration. The sale of fraudulent meat was one of the most widely discussed issues over the past three years, especially during and after the 2013 European horse meat scandal. The scale of the fraud was substantial and led to widespread decline in consumer confidence.

4.1. Concepts of meat adulteration

Meat adulteration can take many forms and there are many points of vulnerability due to complex supply chains. According to Ballin, meat adulteration can be organised into four main areas where fraud is most likely to occur: [130]

1. Meat origin (sex, meat cuts, breed, feed intake, slaughter age, wild vs farmed meat and geographic origin).
2. Meat substitution (species, tissue).
3. Meat processing or treatment (fresh vs thawed, meat preparation)
4. Non-meat ingredient additions (water and additives).

4.2. Meat adulteration using liquid extraction surface-mass spectrometry (LESA-MS)

Montowska et al. undertook the challenge of utilising ambient mass spectrometry to combat meat adulteration. In their early work they attempted to use DESI-MS and liquid extraction surface analysis-mass spectrometry (LESA-MS) to detect meat adulteration. [39] LESA combines micro-liquid extraction from a solid surface with nano-electrospray mass spectrometry. This group stated that there were four key differences between the spectra of DESI-MS and the spectra of LESA-MS: [39]

- The ion intensities in the LESA-MS spectra were one to two orders higher in magnitude compared to DESI-MS.
- A more consistent signal level was observed using LESA-MS.
- LESA-MS produced more multiply charged peptides which meant that there were fewer ions above m/z 1000.
- DESI-MS produced more singly charged peptides which meant that there were ions in the m/z 1000–1600 region.

Both DESI-MS and LESA-MS were used to differentiate between five different meat species; beef, chicken, pork, horse and turkey. Having undertaken data analysis through multivariate statistical software, it was stated that there was better grouping in the LESA-MS models and that the DESI-MS models were weaker, albeit the OPLS-DA plot gave satisfactory separation. It was also stated that LESA-MS gave more reproducible analysis and greater sensitivity compared with DESI-MS, which is in agreement with the findings of Nielsen et al. [27,39] Further work was undertaken by Montowska et al. combining LESA-MS with multivariate data analysis. They were able to clearly discriminate between five different cooked meats (beef, chicken, pork, horse and turkey), as shown in Fig. 1. [40]

Having shown that different cooked meats could be distinguished, the researchers went on to attempt to identify heat stable peptide markers for each type meat. Tryptic digests of raw and cooked meat were analysed using LESA-MS and the peptide markers were identified using targeted MS/MS. Fifteen markers were identified in the cooked meat samples and twenty-nine in the raw meat samples. According to Montowska et al. the reason for the reduced number of markers in the cooked samples was a result of the insolubility of protein aggregates. This was due to the conformational changes of proteins during thermal treatment, resulting in reduced digestion efficiency. [40] Having found heat stable peptide markers, Montowska et al. investigated the levels of detection (LOD) for

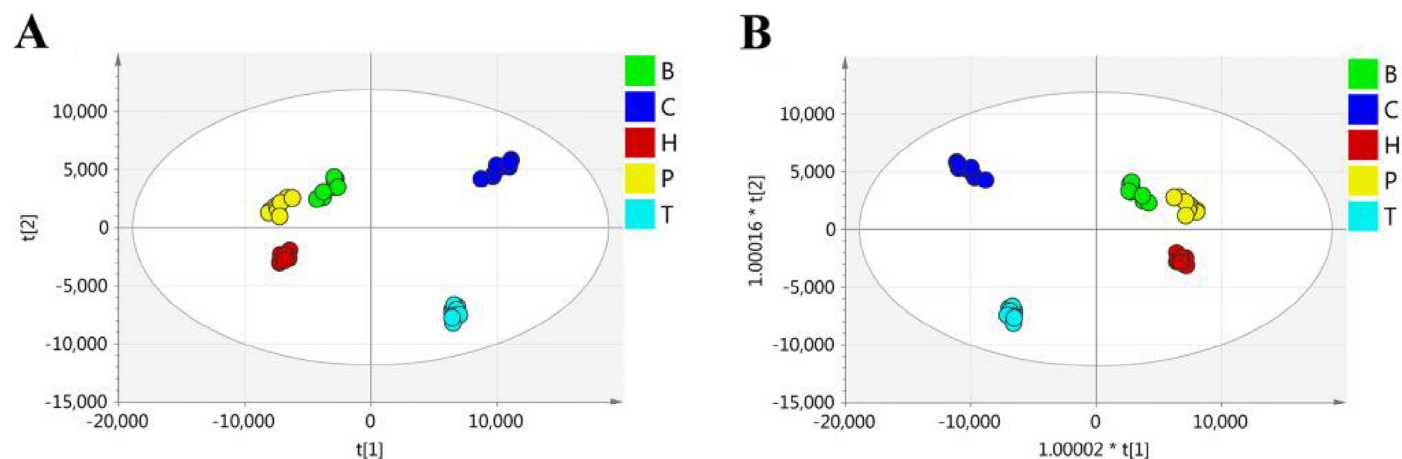


Fig. 1. PCA (left) and OPLS-DA (right) plots, in the range of m/z 400–1000 taken from the work carried out by Montowska et al., demonstrating the clear separation of the five different cooked meats (beef (B), horse (H), pork (P), chicken (C) and turkey (T), using LESA-MS. [40]

Table 5

A table identifying the meat composition of eight of the eighteen processed products analysed by Montowska et al. using LESA-MS. [41]

Sample	Declared meat composition
Potted beef	Beef 67%, beef heart
Hunters sausage	Pork 70%, beef 20%
Kabanos sausage with cheese	Chicken 58%, pork 12%, cheese 7.5%
Pork sausage	Pork 92%, veal 6%
Cocktail sausage	Beef 60%, turkey 6%
Frankfurters poultry	Chicken and Turkey MRM 65%
Frankfurters	Veal 50%, pork 28%
Hotdogs	Pork 40%, chicken 18%

LESA-MS. Samples of cooked beef were prepared and spiked with pork, chicken, turkey and horse meat at concentrations of 10%, 5% and 1%. Once again, using multivariate data analysis, they could easily discriminate between the meat mixtures and demonstrated that LESA-MS successfully detected the peptide markers for horse, pork, chicken and turkey meat at 10 % adulteration. They also detected two chicken peptide markers at 5% adulteration in the beef/chicken sample. [40]

Following this work, Montowska et al. utilised LESA-MS to identify twenty-five species and protein-specific heat stable peptide markers which had been detected in processed samples which had been manufactured from their five target species. [41] Montowska et al. demonstrated that several peptides which were derived from myofibrillar and sarcoplasmic proteins which were resistant to processing. A retail survey was conducted and eighteen meat products were purchased from English and Polish supermarkets. These were tested and it was found that most of the observed peptides were heat stable markers. Using the markers, they were able to declare the meat composition of each product and identified that seven of the processed samples were a mixture of two different meat species, and one sample was found to contain offal, as shown in Table 5.

5. Quantitative analysis

This review has outlined how various AMS techniques (ASAP, DART, DAPCI, EASI, LESA and PS) coupled with mass spectrometry have produced qualitative results which are comparable to those obtained through the use of conventional techniques. There is still some debate as to whether DESI-MS is suited towards detecting the adulteration or fraudulent sale of food as it has been found to be vulnerable to false-positive and false-negative results. [27] Additionally, with the lack of published literature regarding laser based AMS techniques, it is too early to suggest that reliable qualitative results can be achieved. However, food fraud or adulteration procedures cannot be reliant on just obtaining qualitative results. Some aspect of quantification, whether it be semi-quantitative, has to be achieved in order to fully understand the extent of the fraud. A number of food fraud incidents have shown there is a genuine risk to the public's health. The recent example of the identification of ground peanut shells and almond proteins present in ground cumin and paprika required quantification to try and understand the level of risk. [131]

It is believed that food gangs and criminals often attempt to fraudulently sell or adulterate food at levels well above 10%–20% as any smaller amounts of substitution would not lead to substantial economic benefits. It is well known that AMS has been perceived to provide excellent qualitative results but falls some way short in terms of acquiring accurate quantitative results. There are a few publications within this review that have demonstrated scenarios where an AMS technique has obtained quantitative results below 20% adulteration; Vaclavik et al. detected down to 6% adulteration of extra virgin olive oil with hazelnut oil, [81] Shen et al. detected the

adulteration of star anise based teas at levels of 1%, [73] Hrbek et al. detected the adulteration of cheese with plant oils at levels of 1% and Montowska et al. detected chicken in beef samples at levels of 5%. [40,59]

Whereas the majority of food fraud/adulteration studies have only generated semi-quantitative results, and this has been accepted, food safety is a very different issue and quantification of the risk is extremely important. Although this review has focused mainly on the adulteration, traceability and fraudulent sale of food, a small number of cases where food safety is an additional issue have been presented, providing examples of where an AMS technique has successfully obtained quantitative results. Vaclavik et al. successfully detected the presence of melamine and cyanuric acid in milk powder at levels as low as 170 µg/kg and 450 µg/kg respectively using DART-MS and isotopically labelled standards. [61] Using DAPCI-MS, Yang et al. could identify melamine in both milk powder and liquid milk at levels of 1.6×10^{-11} g/mm² and 1.3×10^{-12} g/mm² respectively and Huang et al. could detect melamine at levels of 6–15 µg/kg in milk powder, soy milk powder, liquid milk and synthetic urine when using LTP-MS. [57,62] Zhang et al. could detect melamine in milk powder and infant formula at levels of 20 ng/ml and 50 ng/g respectively, illegal Sudan dyes in chilli powder at levels between 50–100 ng/g and various contaminants in beef and pork samples between 1–5 ng/g using PS-MS. [35] The work undertaken by Fussell et al. using ASAP-MS to detect auramine in saffron also demonstrated some potential signs of quantification when they detected the illegal dye at levels of 8 mg/kg. [29] However, it is clear that ASAP-MS struggles in terms of quantitation, as acknowledged by Fussell et al. and in terms of LOD it is trailing behind the studies using DART-MS, DAPCI-MS, LTP-MS and PS-MS.

At present conventional and AMS techniques are providing similar qualitative results with regards to detecting food fraud. With the fact that the AMS techniques require minimal to no sample preparation and very fast assay running times compared to that of conventional techniques, it is clear that AMS has a major role to play. However, in terms of quantitation there are still big issues concerning how accurate the results are and the possibility for false negative and positive results. Another issue concerning AMS techniques is that the all of the studies which have been shown to provide some levels of quantification are liquid based samples, or solid samples diluted/dissolved in a liquid solution. Thus, perhaps the biggest drawback of all for AMS is that it is not possible to achieve quantification of solid samples. In order to ensure that fit for purpose, reliable and accurate quantification of liquid samples and perhaps solid samples can be achieved by AMS, substantial thought and effort will have to be placed on appropriate quality control procedures as described previously by Hajslova et al. (spiked samples, certified reference materials and comparisons with chromatography based methods). [113] Although their recommendations are specifically described for DART-MS experiments, their suggestions can be extrapolated for any AMS based technique. Until a sufficient number of studies have been carried out operating in accordance with these quality control procedures, it is impossible to know whether AMS can produce both and qualitative and quantitative results.

6. Conclusions

The sale of fraudulent and adulterated food is being reported widely on a global basis and much more frequently than previously. It is clear the driver for such fraud are the large profits that can be achieved. Economically motivated adulteration of food is a common practice that has been carried out since the trading of food commodities began. However, recent scandals such as the adulteration of oregano with olive and myrtle leaves, [80] and more high profile scandals including the European horse meat scandal in 2013 have further highlighted the extent at which it is occurring. The rapid

growth of ambient ionisation techniques coupled with mass spectrometry is exciting with over thirty different techniques now available. Perhaps not all will be capable of detecting the adulteration of food, however, to date a number of these ambient ionisation techniques such as DART, DAPCI, EASI, LESA and PS coupled with mass spectrometry have been proven to enhance and aid the way in which the detection of food adulteration is undertaken. Compared to conventional techniques such as LC-MS, NMR, ELISA, PCR and various spectroscopic techniques which were commonly used to investigate the adulteration of food, the authenticity and traceability of food and general food safety, these ambient mass spectrometry techniques require no sample preparation and minimal sampling time thus producing fast and accurate results which most importantly are comparable with results obtained from conventional techniques. It is clear there is rapid growth in the use of ambient mass spectrometry applied to food adulteration issues. It appears to be an area of analytical chemistry that lends itself to the needs of regulators and industry, and may become one of the most important analytical tools in detecting food fraud globally.

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References

- [1] Department for Environment, Food and Rural Affairs, Food Statistics Pocketbook. <https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/423616/foodpocketbook-2014report-23apr15.pdf>, 2014, accessed 13.06.2016.
- [2] Institute of Grocery Distribution, UK Grocery Retailing. <<http://www.igd.com/Research/Retail/retail-outlook/3371/UK-Grocery-Retailing/>>, 2015, accessed 13.06.2016.
- [3] Horizons, UK foodservice sector set to be worth £56.3bn by 2019 hears horizons' Annual Briefing. <<http://www.hrzns.com/news/uk-foodservice-worth-56bn-2019>>, 2015, accessed 13.06.2016.
- [4] K. Johnson, Institute of Grocery Distribution. <<http://www.igd.com/Research/Retail/retail-outlook/29358/2020-global-grocery-market-forecasts/>>, 2015, accessed date 13.06.2016.
- [5] J. Spink, D.C. Moyer, Food Technol. 67 (2013) 30.
- [6] J. Spink, D.C. Moyer, J. Food Sci. 76 (2011) R157.
- [7] R. Johnson, Congressional Research Service, Food Fraud and "economically motivated adulteration" of food and food ingredients. <<https://www.fas.org/sgp/crs/misc/R43358.pdf>>, 2014, accessed date 13.06.2016.
- [8] Institute of Grocery Distribution, Global Market Sizes 2015–2020. 2015.
- [9] J. Spink, Anonymous Improving Import Food Safety, John Wiley & Sons, Inc, Hoboken, NJ, USA, 2012, pp. 195–216.
- [10] D.L. Heyman, A safer future. <http://www.who.int/whr/2007/whr07_en.pdf>, 2007, accessed 13.06.2016.
- [11] J. Li, X. Ding, D. Liu, F. Guo, Y. Chen, Y. Zhang, et al., J. Chromatogr. B. Anal. Technol. Biomed. Life Sci. 942–943 (2013) 46.
- [12] J. Glotz, Fairtrade and organic fakes 'could be next fraud scandal', May ed., The Grocer, Crawley, 2015, p. 4.
- [13] D.I. Ellis, V.L. Brewster, W.B. Dunn, J.W. Allwood, A.P. Golovanov, R. Goodacre, Chem. Soc. Rev. 41 (2012) 5706.
- [14] L.M. Reid, C.P. O'Donnell, G. Downey, Trends Food Sci. Technol. 17 (2006) 344.
- [15] I. Reinholds, V. Bartkevics, I.C.J. Silvis, S.M. van Ruth, S. Esslinger, J. Food Compos. Anal. 44 (2015) 56.
- [16] M. Castro-Puyana, M. Herrero, Trends Anal. Chem. 52 (2013) 74.
- [17] E.J. Want, P. Masson, F. Michopoulos, I.D. Wilson, G. Theodoridis, R.S. Plumb, et al., Nat. Protoc. 8 (2013) 17.
- [18] R.C. De Vos, S. Moco, A. Lommen, J.J. Keurentjes, R.J. Bino, R.D. Hall, Nat. Protoc. 2 (2007) 778.
- [19] A. Venter, M. Neffiu, R.G. Cooks, TrAC-Trends Anal. Chem. 27 (2008) 284.
- [20] J.B. Fenn, Method and apparatus for electrospray ionization, US 6297499 B1, 1998.
- [21] H. Wang, J. Liu, R.G. Cooks, Z. Ouyang, Angew. Chem. Int. Ed. 49 (2010) 877.
- [22] Z. Takáts, J.M. Wiseman, B. Gologan, R.G. Cooks, Science (Classic) 306 (2004) 471.
- [23] M. Huang, S. Cheng, Y. Cho, J. Shiea, Anal. Chim. Acta 702 (2011) 1.
- [24] Z. Takáts, J.M. Wiseman, R.G. Cooks, J. Mass Spectrom. 40 (2005) 1261.
- [25] R.B. Cody, J.A. Laramée, H.D. Durst, Anal. Chem. 77 (2005) 2297.
- [26] C.N. McEwen, R.G. McKay, B.S. Larsen, Anal. Chem. 77 (2005) 7826.
- [27] M.W.F. Nielen, H. Hooijerink, P. Zomer, J.G.J. Mol, TrAC-Trends Anal. Chem. 30 (2011) 165.
- [28] M. Doué, G. Dervilly-Pinel, A. Gicquiau, K. Pouponneau, F. Monteau, B. Le Bizet, Anal. Chem. 86 (2014) 5649.
- [29] R.J. Fussell, D. Chan, M. Sharman, TrAC-Trends Anal. Chem. 29 (2010) 1326.
- [30] D.J. Weston, Analyst 135 (2010) 661.
- [31] L. Li, B. Feng, J. Yang, C. Chang, Y. Bai, H. Liu, Analyst 138 (2013) 3097.
- [32] L. Nyadong, A.S. Galhena, F.M. Fernández, Anal. Chem. 81 (2009) 7788.
- [33] A.S. Galhena, G.A. Harris, L. Nyadong, K.K. Murray, F.M. Fernández, Anal. Chem. 82 (2010) 2178.
- [34] T. Cajka, H. Danhelova, M. Zachariasova, K. Riddellova, J. Hajslova, Metabolomics 9 (2013) 545.
- [35] Z. Zhang, R.G. Cooks, Z. Ouyang, Analyst 137 (2012) 2556.
- [36] B. Kuswandi, K. Cendekiawan, N. Kristiningrum, M. Ahmad, J. Food Measure. Character. 9 (2015) 313.
- [37] C.A. Quinto, R. Tinoco, R.S. Hellberg, Food Control 59 (2016) 386.
- [38] Y.P. Hsieh, J.A. Ofori, J. Agric. Food Chem. 62 (2014) 12536.
- [39] M. Montowska, W. Rao, M.R. Alexander, G.A. Tucker, D.A. Barrett, Anal. Chem. 86 (2014) 4479.
- [40] M. Montowska, M.R. Alexander, G.A. Tucker, D.A. Barrett, Anal. Chem. 86 (2014) 10257.
- [41] M. Montowska, M.R. Alexander, G.A. Tucker, D.A. Barrett, Food Chem. 187 (2015) 297.
- [42] E. Streit, C. Schwab, M. Sulyok, K. Naehrer, R. Krska, G. Schatzmayr, Toxins (Basel) 5 (2013) 504.
- [43] S.W. Erasmus, M. Muller, M. van der Rijst, L.C. Hoffman, Food Chem. 192 (2016) 997.
- [44] I. Boyaci, R. Uysal, H. Temiz, E. Shendi, R. Yadegari, M. Rishkan, et al., Eur. Food Res. Technol. 283 (2014) 845.
- [45] S. Chen, M. Hoene, J. Li, Y. Li, X. Zhao, H. Häring, et al., J. Chromatogr. A 1298 (2013) 9.
- [46] G.D. Fernandes, M. Wenceslao, D. Barrera-Arellano, G.C.N.Z. Ruiz, P.L. Ferreira, M.N. Eberlinc, et al., J. Braz. Chem. Soc. 25 (2014) 1565.
- [47] T. Cajka, H. Danhelova, A. Vavrecka, K. Riddellova, V. Kocourek, F. Vacha, et al., Talanta 115 (2013) 263.
- [48] Z. Wu, H. Chen, W. Wang, B. Jia, T. Yang, Z. Zhao, et al., J. Agric. Food Chem. 57 (2009) 9356.
- [49] A.M. Porcari, G.D. Fernandes, K.R.A. Belaz, N.V. Schwab, V.G. Santos, R.M. Alberici, et al., Anal. Methods 6 (2014) 2436.
- [50] A.M. Porcari, N.V. Schwab, R.M. Alberici, E.C. Cabral, D.R. de Moraes, P.F. Montanher, et al., Anal. Methods 4 (2012) 3551.
- [51] A. Galal-Khalla, A. Ardura, K. Mohammed-Geba, Y.J. Borrell, E. Garcia-Vazquez, Food Control 46 (2014) 441.
- [52] H.M. Velioglu, H.T. Temiz, I.H. Boyaci, Food Chem. 172 (2015) 283.
- [53] A. Anater, L. Manyes, G. Meca, E. Ferrer, F.B. Luciano, C.T. Pimpão, et al., Aquaculture 451 (2016) 1.
- [54] C. Alamprese, E. Casiraghi, LWT Food Sci. Technol. 63 (2015) 720.
- [55] L. Taboada, A. Sánchez, A. Velasco, F.J. Santaclara, R.I. Pérez-Martín, C.G. Sotelo, J. Agric. Food Chem. 62 (2014) 5699.
- [56] S.J. Rochford, V. Ezernieks, A.D. Maher, B.A. Ingram, L. Olsen, Food Res. Int. 54 (2013) 1302.
- [57] S. Yang, J. Ding, J. Zheng, B. Hu, J. Li, H. Chen, et al., Anal. Chem. 81 (2009) 2426.
- [58] L. Zhang, W. Yong, J. Liu, S. Wang, Q. Chen, T. Guo, et al., J. Am. Soc. Mass Spectrom. 26 (2015) 1414.
- [59] V. Hrbek, L. Vaclavik, O. Elich, J. Hajslova, Food Control 36 (2014) 138.
- [60] A.J. Dane, R.B. Cody, Analyst 135 (2010) 696.
- [61] L. Vaclavik, J. Rosmus, B. Popping, J. Hajslova, J. Chromatogr. A 1217 (2010) 4204.
- [62] G. Huang, Z. Ouyang, R.G. Cooks, Chem. Commun. (Cambridge) 556 (2009) 2009.
- [63] P.M. Santos, E.R. Pereira-Filho, L.A. Colnago, Microchem. J. 124 (2016) 15.
- [64] P.M. Santos, E.R. Pereira-Filho, L.E. Rodriguez-Saona, Food Chem. 138 (2013) 19.
- [65] C. Agrimonti, A. Pirondini, M. Marmiroli, N. Marmiroli, Food Chem. 187 (2015) 58.
- [66] L. Donghua, P. Yuanyuan, Z. Hui, Trans. Chin. Soc. Agric. Eng. 30 (2014) 238.
- [67] Q.R. Ren, H. Zhang, H.Y. Guo, L. Jiang, M. Tian, F.Z. Ren, J. Dairy Sci. 97 (2014) 6000.
- [68] N.M. Suni, H. Aalto, T.J. Kauppila, T. Kotiaho, R. Kostiainen, J. Mass Spectrom. 47 (2012) 611.
- [69] S. Gerbig, Z. Takáts, Rapid Commun. Mass Spectrom. 24 (2010) 2186.
- [70] R. Russo, V. Severino, A. Mendez, J. Libreria, A. Parente, A. Chambery, J. Mass Spectrom. 47 (2012) 1407.
- [71] N.A. Fadzillah, Y.B. Che Man, A. Rohman, A.S. Rosman, A. Ismail, S. Mustafa, et al., J. Oleo Sci. 64 (2015) 697.
- [72] H. Chen, J. Zheng, X. Zhang, M. Luo, Z. Wang, X. Qiao, J. Mass Spectrom. 42 (2007) 1045.
- [73] Y. Shen, T.A. van Beek, F.W. Claassen, H. Zuilhof, B. Chen, M.W.F. Nielen, J. Chromatogr. A 1259 (2012) 179.
- [74] B. Avula, T.J. Smillie, Y. Wang, J. Zweigenbaum, I.A. Khan, Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess. 32 (2015) 1.
- [75] D. Taverna, L. Di Donna, F. Mazzotti, B. Policicchio, G. Sindona, J. Mass Spectrom. 48 (2013) 544.
- [76] S.A. Haughey, P. Galvin-King, Y. Ho, S.E.J. Bell, C.T. Elliott, Food Control 48 (2015) 75.
- [77] M. Bononi, I. Fiordaliso, F. Tateo, Ital. J. Food Sci. 22 (2010) 479.
- [78] M. Bononi, F. Tateo, Ital. J. Food Sci. 23 (2011) 245.

- [79] Y. Wang, H. Jin, S. Ma, J. Lu, R. Lin, J. Chromatogr. A 1218 (2011) 334.
- [80] C. Black, S.A. Haughey, O.P. Chevallier, P. Galvin-King, C.T. Elliott, Food Chem. 210 (2016) 551.
- [81] L. Vaclavik, T. Cajka, V. Hrbek, J. Hajslova, Anal. Chim. Acta 645 (2009) 56.
- [82] M.F. Riccio, A.C.H.F. Sawaya, P.V. Abdelnur, S.A. Saraiva, R. Haddad, M.N. Eberlin, et al., Anal. Lett. 44 (2011) 1489.
- [83] J. Liu, B. Qiu, H. Luo, Rapid Commun. Mass Spectrom. 24 (2010) 1365.
- [84] F. Mazzotti, L. Di Donna, D. Taverna, M. Nardi, D. Aiello, A. Napoli, et al., Int. J. Mass Spectrom. 352 (2013) 87.
- [85] H. Jabeur, A. Zribi, M. Bouaziz, Food Anal. Method. 9 (2015) 712.
- [86] M. Bougrini, K. Tahri, Z. Haddi, T. Saidi, N.E. Bari, B. Bouchikhi, J. Sensor. 2014 (2014) 1.
- [87] G. Papotti, D. Bertelli, R. Graziosi, A. Maietti, P. Tedeschi, A. Marchetti, et al., LWT Food Sci. Technol. 60 (2015) 1017.
- [88] R. Moscetti, E. Radicetti, D. Monarca, M. Cecchini, R. Massantini, J. Sci. Food Agric. 95 (2015) 2619.
- [89] L. Vaclavik, M. Zachariasova, V. Hrbek, J. Hajslova, Talanta 82 (2010) 1950.
- [90] E. Alexa, D. Bordean, A. Cimpean, C.A. Dehelean, M. Poiana, G. Pop, et al., Chem. Cent. J. 7 (2013) 1.
- [91] N. Pang, T. Wang, J. Hu, Food Chem. 190 (2016) 793.
- [92] K. Mastovska, K.J. Dorweiler, S.J. Lehotay, J.S. Wegscheid, K.A. Szpylka, J. Agric. Food Chem. 58 (2010) 5959.
- [93] J.S. Wiley, J.F. García-Reyes, J.D. Harper, N.A. Charipar, Z. Ouyang, R.G. Cooks, Analyst 135 (2010) 971.
- [94] H. Evard, A. Krueve, R. Löhms, I. Leito, J. Food Compost Anal. 41 (2015) 221.
- [95] B. Gilbert-López, J.F. García-Reyes, C. Meyer, A. Michels, J. Franzke, A. Molina-Díaz, et al., Analyst 137 (2012) 5403.
- [96] H. Novotná, O. Kmiecik, M. Galazka, V. Krtková, A. Hurajová, V. Schulzová, et al., Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess. 29 (2012) 1335.
- [97] X. Mi, J. Yang, L. Cao, X. Wei, Y. Zhu, Q. Li, et al., Food Res. Int. 76 (2015) 926.
- [98] A.P. Sobolev, L. Mannina, N. Proietti, S. Carradori, M. Daglia, A.M. Giusti, et al., Molecules 20 (2015) 4088.
- [99] N. Fleury-Filho, C.A. Nascimento, E.O. Faria, A.R. Crunivel, J.M. Oliveria, Food Addit. Contam. 29 (2012) 641.
- [100] T. Cajka, K. Riddellova, M. Tomaniova, J. Hajslova, J. Chromatogr. A 1217 (2010) 4195.
- [101] T. Cajka, K. Riddellova, M. Tomaniova, J. Hajslova, Metabolomics 7 (2011) 500.
- [102] M. Beneito-Cambra, P. Pérez-Ortega, A. Molina-Díaz, J.F. García-Reyes, Anal. Methods 7 (2015) 7345.
- [103] J. Liu, H. Wang, N.E. Manicke, J. Lin, R.G. Cooks, Z. Ouyang, Anal. Chem. 82 (2010) 2463.
- [104] R. Garrett, C.M. Rezende, D.R. Iffa, Anal. Methods 5 (2013) 5944.
- [105] R. Garrett, N.V. Schwab, E.C. Cabral, B.V.M. Henrique, D.R. Iffa, M.N. Eberlin, et al., J. Braz. Chem. Soc. 25 (2014) 1172.
- [106] N. Dordevic, F. Camin, R.M. Marianella, G.J. Postma, L.M.C. Buydens, R. Wehrens, Aust. J. Grape Wine Res. 19 (2013) 324.
- [107] D. Markechová, P. Májek, J. Sádecká, Food Chem. 159 (2014) 193.
- [108] P. Wiśniewska, T. Dymerski, W. Wardencki, J. Namieśnik, J. Sci. Food Agric. 95 (2015) 2159.
- [109] T. Cai, H. Ting, Z. Jin-Lan, Food Chem. 190 (2016) 1046.
- [110] J. Wang, W. Chow, D. Leung, J. AOAC Int. 94 (2011) 1685.
- [111] M.W.F. Nielen, H. Hooijerink, F.C. Claassen, M.C. van Engelen, T.A. van Beek, Anal. Chim. Acta 637 (2009) 92.
- [112] A.F.M.M. Rahman, R.F. Angawi, A.A. Kadi, Food Chem. 173 (2015) 489.
- [113] J. Hajslova, T. Cajka, L. Vaclavik, TrAC-Trends Anal. Chem. 30 (2011) 204.
- [114] C.E. Handford, K. Campbell, C.T. Elliott, Compr. Rev. Food Sci. F. 15 (2016) 130.
- [115] N.K. Andrikopoulos, I.G. Giannakis, V. Tzamtzis, J. Chromatogr. Sci. 39 (2001) 137.
- [116] N. Ogrinc, I.J. Kosir, J.E. Spangenberg, J. Kidric, Anal. Bioanal. Chem. 376 (2003) 424.
- [117] L. Laboureur, M. Ollero, D. Touboul, Int. J. Mol. Sci. 16 (2015) 13868.
- [118] European Commission, EU No 1130/2011, <<https://www.food.gov.uk/science/additives/enumerlist>>, 2014, accessed 13.06.2016.
- [119] T.A. Apekey, S. Khokhar, Survey on the consumption of cinnamon-containing foods and drinks by the UK population, FSA report, 2010, <<http://www.food.gov.uk/science/research/chemical-safety-research/additives-research/a01073>>, 2015, accessed 13.06.2016.
- [120] Waters Corporation, <<http://www.waters.com/webassets/cms/library/docs/720003274en.pdf>>, 2010, accessed date 13.06.2016.
- [121] S. Ju, C. Han, C. Wu, A.M. Mebel, Y. Chen, J. Phys. Chem. B. 103 (1999) 582–596.
- [122] X. Ren, J. Liu, C. Zhang, H. Luo, Rapid Commun. Mass Spectrom. 27 (2013) 613.
- [123] A.M. Porcari, G.D. Fernandes, D. Barrera-Arellano, M.N. Eberlin, R.M. Alberici, Analyst 141 (2016) 1172.
- [124] R. Haddad, H.M.S. Milagre, R. Ramos Catharino, M.N. Eberlin, Anal. Chem. 80 (2008) 2744.
- [125] C.W. Klampfl, M. Himmelsbach, Anal. Chim. Acta 890 (2015) 44.
- [126] International Coffee Organisation, <<http://www.ico.org/prices/production.pdf>>, 2015, accessed date 13.06.2016.
- [127] International Coffee Organisation, <<http://www.ico.org/prices/m1-exports.pdf>>, 2015, accessed date 13.06.2016.
- [128] International Coffee Organisation, <<http://www.ico.org/prices/m4-imports.pdf>>, 2015, accessed date 13.06.2016.
- [129] J. Sampson, K. Murray, D. Muddiman, J. Am. Soc. Mass Spectrom. 20 (2009) 667.
- [130] N.Z. Ballin, Meat Sci. 86 (2010) 577.
- [131] The Seasoning and Spice Association, <<http://www.seasoningandspice.org.uk/publicgeneral/Q&A.pdf>>, 2016, accessed date 13.06.2016.